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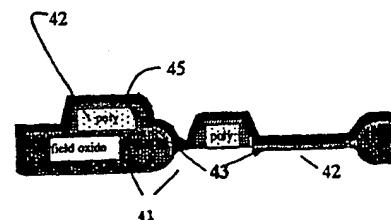
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<p>(21) International Application Number: PCT/BE00/00045</p> <p>(22) International Filing Date: 28 April 2000 (28.04.00)</p> <p>(30) Priority Data: 60/132,284 3 May 1999 (03.05.99) US</p> <p>(71) Applicants (for all designated States except US): INTERUNIVERSITAIR MICROELEKTRONICA CENTRUM (IMEC) [BE/BE]; Kapeldreef 75, B-3001 Leuven (BE). DOW CORNING CORPORATION [US/US]; 2200 W. Salzburg Road, P.O. Box 994, Midland, MI 48686-0994 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): VANHAELEMEERSCH, Serge [BE/BE]; Kapelberg 56, B-3001 Leuven (BE). MEYNEN, Herman [BE/BE]; Hazenpad 15, B-3210 Linden (BE). DEMBOWSKI, Philip, David [US/US]; 6106 Briarwood Ct., Midland, MI 48640-1966 (US).</p> <p>(74) Agents: VAN MALDEREN, Joëlle et al.; Office Van Malderen, Place Reine Fabiola 6/1, B-1083 Brussels (BE).</p>	<p>(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	

(54) Title: METHOD FOR REMOVAL OF SiC

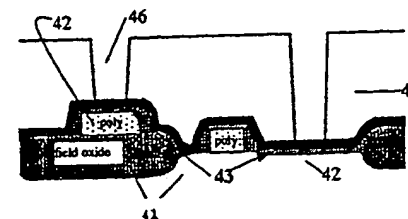
(57) Abstract

The present invention is related to a method for removal of silicon carbide layers and in particular amorphous SiC of a substrate comprising the steps of: converting at least partly said exposed part of said carbide-silicon layer into an oxide-silicon layer by exposing said carbide-silicon layer to an oxygen containing plasma; and removing said oxide-silicon layer from said substrate. The present invention is also related to an integrated circuit implementing said method.

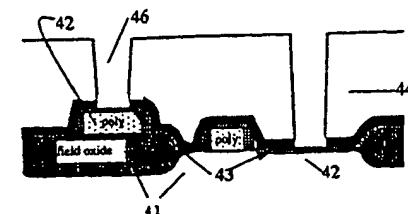
Step a)



Step b)



Step c) and d)



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METHOD FOR REMOVAL OF SiC

Field of the invention

10 [0001] The present invention is related to a method for removal of silicon carbide layers and in particular amorphous SiC of a substrate.

[0002] The present invention is also related to an integrated circuit implementing said method.

15

Background of the invention

[0003] SiC (Silicon Carbide), particularly amorphous SiC, is known as a chemically very stable component. In semiconductor processing, many modules, defined as a set of
20 subsequent basic steps, require the presence of a thin layer which remains substantially unaffected by the operation being performed, i.e. so-called semi-inert layers. Particularly, such a semi-inert layer can be used as a hard mask layer during dry etch, or as an etch stop
25 layer during wet/dry etch, or as stopping layer for a Chemical-Mechanical polishing process (CMP) or for many other applications. For instance, these semi-inert layers can also be used as diffusion barrier layers. Due to its high chemical stability, the use of a SiC layer as a
30 semi-inert layer may have benefits over other materials such as silicon dioxide and silicon nitride, especially for those applications where selectivity to the operation being performed is of high importance for successful implementation. In addition, SiC layers may be superior in
35 terms of barrier properties.

[0004] Document US-A-5,818,071 is related to interconnect structures incorporating a silicon carbide layer as a diffusion barrier layer particularly between a dielectric and a highly conductive metal layer with a
5 resistivity less than about 2.5 microhm-centimetres. Document US-A-5,818,071 does not disclose the use of a silicon carbide layer as an etch stop layer and a diffusion barrier layer in pre-metal dielectric structures, particularly between a silicide layer and a dielectric. US
10 5818071 does not disclose how to pattern or to remove the silicon carbide layer selectively to the underlying layer, in casu a metal layer.

[0005] Although a silicon carbide layer is a very attractive layer to use in semiconductor processing and
15 particularly in interconnect structures and dielectric structures, its high chemical stability can also be its biggest disadvantage. SiC suffers from the fact that it is very difficult (if not impossible at all) to remove and particularly to remove it selectively. Some examples of
20 process flows where such removal is required are: the stopping layers in the CMP operations for definition of field area's using the shallow trench isolation approach; and the use as etch stop layers for contact and via definition, where the process flow requires the selective
25 removal of the etch stop layer at the bottom of the contact/via to obtain low contact/via resistance. Another example is also related to the use of SiC as a stopping layer in CMP applications. The cleaning after CMP usually relies on under-etching of the particles/residues. This
30 requires that the surface from which particles and/or residues need to be removed can be etched isotropically in a very controlled way. However, due to the high chemical stability of SiC, particles and/or residues on top of the SiC layer can not be under-etched and therefore, cleaning
35 becomes rather difficult.

[0006] Document EP-A-0845803 discloses the removal of a surface portion of a crystalline SiC film. First, defects are introduced in the top layer, thereafter, the

top layer is converted into a silicon oxide layer by a thermal oxidation treatment typically at a temperature of 1100°C. This renders this process unsuited for use in interconnect structures and pre-metal dielectric (PMD) structures because active devices are already defined and therefore only limited thermal treatments can be applied, i.e. typically 600°C or below. Moreover, the silicide layers in the PMD structures, are also not compatible with temperatures above 650°C, while most metal features in the interconnect structures are not compatible with temperatures typically above about 400°C.

Aims of the invention

[0007] It is an aim of the invention to remove exposed layers of a SiC layer by converting at least a major part of said SiC layer in silicon (di)oxide or silicon oxide based layers. Particularly this conversion is performed at low temperatures, preferably 600°C or below, in an oxygen-containing plasma. Thereafter the converted part of said SiC layer is removed.

[0008] It is a further aim of the invention to provide a method for fabricating an interconnect structures, including PMD structures, using SiC as etch stop layer and/or diffusion barrier layer by using the afore-mentioned method for in-situ selective removal of exposed layers of the SiC layer.

[0009] It is still a further aim of the invention to provide an interconnect structure, particularly a PMD structure wherein a SiC layer can be used as an etch stop layer between a conductive layer and the surrounding dielectric.

Summary of the invention

[0010] This invention is about the selective removal of exposed layers of SiC layers which allows the use of this highly chemically stable material for a wide range of

applications. At least for the purpose of this disclosure a carbide-silicon layer is an insulating layer being composed of at least Si and C, e.g., but not limited hereto, SiC, or at least Si, C and O, e.g. silicon oxycarbide, or at least
5 Si, C and N, e.g. nitrided silicon carbide (SiNC) or at least Si, N, O and C, e.g. nitrided silicon oxycarbide (SiNOC), or at least Si, C and H e.g. amorphous hydrogenated silicon carbide (SiC:H), or at least Si, C, N and H, e.g. hydrogenated SiNC, or at least Si, O, C, N and
10 H, e.g. hydrogenated SiNOC. For the purpose of this disclosure, an oxide-silicon layer is a layer composed of at least Si and O, e.g. silicon (di)oxide, or of Si, O and a smaller fraction of C and /or a smaller fraction of N and/or a smaller fraction of H, for example silicon
15 (di)oxide wherein the fraction of C and/or N and/or H smaller is than the fraction of O.

[0011] In an aspect of the invention, a method for removing at least partly an exposed part of a carbide-silicon layer formed on a substrate is disclosed comprising
20 the steps of :

- converting at least partly said exposed part of said carbide-silicon layer into an oxide-silicon layer by exposing said carbide-silicon layer to an oxygen containing plasma,
- 25 - removing said oxide-silicon layer from said substrate.

[0012] Said exposed part can be, but is not limited hereto, an exposed part in an opening or can be at least an exposed part of a layer.

30 [0013] This method can be applied in-situ. The substrate can be, but is not limited hereto, a partly processed or a pristine wafer or slice of a semi-conductive material, like Si or Ga As or Ge, or an insulating material, e.g. a glass slice, or a conductive material.
35 Said substrate can comprise a patterned conductive layer. Particularly, in case said substrate is a partly processed wafer or slice; at least a part of the active and/or passive devices can already be formed and/or at least a

part of the structures interconnecting these devices can be formed.

[0014] For the purpose of this disclosure, plasma should be understood as a conventional plasma such as a reactive ion etch (RIE) plasma or a chemical vapour deposition (CVD) plasma, or a plasma afterglow. By exposing said carbide-silicon layer to an oxygen-containing plasma, energy is given to the oxygen containing species, such that carbide-silicon is at least partly converted into oxide-silicon. This energy can be e.g. thermal energy or kinetic energy, e.g. by the formation of ions.

[0015] In an embodiment of the invention, a method as recited in the first aspect of this invention is disclosed, wherein said conversion step and said removal step are subsequently repeated for a number of times until said carbide-silicon layer is substantially removed.

[0016] In an embodiment of the invention, the conversion from a part of the carbide-silicon layer to an oxide-silicon layer can be performed by exposing the carbide-silicon layer to an oxygen-containing reactive ion etch (RIE) plasma. Particularly, the substrate including the carbide-silicon layer can be introduced in a pressurised chamber of a plasma-etch tool. The pressure can be lower than 3 Torr and preferably between 1 mTorr and 1 Torr. The temperature in said chamber can be 300°C or below; or preferably below 100°C. This temperature can also be in the range from -20°C to 100°C. Preferably, said temperature is about room temperature. The energy of the RIE plasma can be between 1 eV and 500 eV, such that ionic species can be formed.

[0017] In another embodiment, the conversion from a part of the carbide-silicon layer to an oxide-silicon layer can be performed by exposing the carbide-silicon layer to an oxygen-containing CVD plasma. The substrate including the carbide-silicon layer can be introduced in a pressurised chamber of a chemical vapour deposition tool. The pressure can be, but is not limited hereto, higher than 5 Torr, e.g. 10 Torr. The temperature can be in the range

between 250°C and 550°C, preferably in the range between 350°C and 500°C.

[0018] In yet another embodiment of the invention, the conversion from a part of the carbide-silicon layer to an oxide-silicon layer can be performed by exposing the carbide-silicon layer to an oxygen-containing plasma afterglow. Particularly, the substrate including the carbide-silicon layer can be introduced in a pressurised chamber of a plasma tool. Said plasma afterglow can be characterised, but is not limited hereto, by a pressure in the range from 0.02 Torr to 3 Torr, and in the range between 0.2 Torr and 1.5 Torr and preferably between 0.75 Torr and 1.25 Torr, e.g. about 0.85 Torr or about 1.1 Torr. The flow of the oxygen containing substance can be lower than 10000 Sccm and preferably, but not limited hereto, about 4000 Sccm.

[0019] The temperature in said chamber is preferably 600°C or below. This temperature can also be in the range from 100 to 600°C and also in the range from 200 to 400°C and also in the range from 200 to 300°C. This temperature is preferably, but not limited hereto, about 230°C.

[0020] In another aspect of the invention, an integrated circuit on a substrate with at least one conductive layer being partly exposed is disclosed, said circuit comprising:

- a conductive layer deposited on a semiconducting layer,
- at least one dielectric layer having at least one opening extending through said dielectric layer to expose at least a part of said conductive layer,
- a carbide-silicon layer being formed at least on said conductive layer and being positioned between said dielectric layer and said conductive layer adjacent to said exposed part of said conductive layer.

[0021] Said conductive layer can be a pure metal or a metal alloy of the group of metals consisting of Al, Cu, W, Pt, Ag, Ni, Au, Co, Ti, Ta; or a Si-containing or other semiconductor-containing layer such as, but not limited

hereto, e.g. a silicide, a polysilicon or a silicon layer. Said semiconducting layer can be a silicon containing layer, a GaAs layer, a Ge layer or a SiGe layer. Said dielectric layer has preferably a dielectric constant of
5 less than about 4.

[0022] In an embodiment the invention an integrated circuit comprising an interconnect structure on a substrate having a surface with at least one exposed Si-containing layer, particularly a PMD structure, is disclosed. This
10 interconnect structure further comprises:

- a conformal silicide layer on said exposed Si-containing layer;
- at least one dielectric layer on said surface of said substrate having at least one opening, said
15 opening extending through said dielectric layer to thereby define an exposed part of said silicide layer; and
- a carbide-silicon layer being formed at least on said silicide layer and being positioned between said dielectric layer and said silicide layer adjacent to
20 said exposed part of said silicide layer.

[0023] A silicide layer can be a compound comprising silicon and at least one of the group comprising Co, Ti, Ta, Co, Mb, Ni, Pt and W.

[0024] In yet a further aspect of the invention, a
25 method for fabricating an integrated circuit on a substrate having a surface with at least one conductive layer on a semiconducting layer is disclosed. This conductive layer can be a pure metal or a metal alloy of the group of metals consisting of Al, Cu, W, Pt, Ag, Ni, Au, Co, Ti, Ta; or a
30 Si-containing or other semiconductor-containing layer such as, but not limited hereto, e.g. a silicide, a polysilicon or a silicon layer.

[0025] This method comprises the steps of:
- forming a carbide-silicon layer at least on
35 said conductive layer;
- depositing at least one dielectric layer on said surface and on said carbide-silicon layer;

- forming at least one opening in said dielectric layer extending through said dielectric layer to thereby expose a part of said carbide-silicon layer formed on said conductive layer;

5 - in-situ converting said exposed part of said carbide-silicon layer in said opening into a oxide-silicon layer by exposing said exposed part of said carbide-silicon layer in said opening to an oxygen-containing plasma; and

10 - removing said oxide-silicon layer in said opening.

[0026] Said conversion step and said removal step can subsequently be repeated for a number of times until at least a part of said conductive layer is exposed.

15

Short description of the drawings

[0027] Fig. 1 depicts ellipsometric measurements performed on two different amorphous hydrogenated silicon carbide layers being a layer of 20 nm (2) and a layer of
20 50 nm (1) at different time periods being before (partly) conversion to a oxide-silicon layer (3) according to an embodiment of the invention, from the onset of this conversion (3) till the removal of the converted part (4), and after the removal of the oxide-silicon layer (5).

25 [0028] Fig. 2 depicts the thickness of a carbide-silicon layer which is partly converted into an oxide-silicon, according to an embodiment of the present invention, versus the etch time using a HF based etch solution.

30 [0029] Fig. 3 depicts a schematic representation of a pre-metal dielectric structure according to an embodiment of the invention.

[0030] Fig. 4 depicts some processing steps applied to obtain a pre-metal dielectric structure according to an
35 embodiment of the invention.

Detailed description of the invention

[0031] In relation to the appended drawings the present invention is described in details in the sequel. It is apparent however that a person skilled in the art can
5 imagine several other equivalent embodiments or other ways of executing the present invention, the spirit and scope of the present invention being limited only by the terms of the appended claims.

[0032] At least for the purpose of this disclosure a
10 carbide-silicon layer is an insulating layer being composed of at least Si and C, e.g., but not limited hereto, SiC, or at least Si, C and O, e.g. silicon oxycarbide, or at least Si, C and N, e.g. nitrided silicon carbide (SiNC) or at
15 least Si, N, O and C, e.g. nitrided silicon oxycarbide (SiNOC), or at least Si, C and H e.g. amorphous hydrogenated silicon carbide (SiC:H), or at least Si, C, N and H, e.g. hydrogenated SiNC, or at least Si, O, C, N and H, e.g. hydrogenated SiNOC. For the purpose of this disclosure, an oxide-silicon layer is a layer composed of
20 at least Si and O, e.g. silicon (di)oxide, or of Si, O and a smaller fraction of C and /or a smaller fraction of N and/or a smaller fraction of H, for example silicon (di)oxide wherein the fraction of C and/or N and/or H smaller is than the fraction of O. Said oxide-silicon layer
25 comprises at least one of the group consisting of silicon dioxide, silicon dioxide with a smaller fraction of C, silicon dioxide with a smaller fraction of N and C, silicon dioxide with a smaller fraction of N, hydrogenated silicon dioxide, hydrogenated silicon dioxide with a smaller
30 fraction of C, hydrogenated silicon dioxide with a smaller fraction of N and C and hydrogenated silicon dioxide with a smaller fraction of N.

[0033] In an embodiment of the invention, an object is to remove an exposed part of a carbide-silicon layer in-
35 situ by converting at least partly said exposed part of said carbide-silicon layer into an oxide-silicon. The disclosed method comprises the steps converting at least partly said exposed part of said carbide-silicon layer into

an oxide-silicon layer by exposing said carbide-silicon layer to an oxygen containing plasma and removing said oxide-silicon layer from said substrate. Said conversion step and said removal step can be subsequently repeated for
5 a number of times until said carbide-silicon layer is substantially removed.

[0034] Said exposed part can be, but is not limited hereto, an exposed part in an opening or can be at least an exposed part of a layer.

10 [0035] This method can be applied in-situ. The substrate can be, but is not limited hereto, a partly processed or a pristine wafer or slice of a semi-conductive material, like Si or Ga As or Ge, or an insulating material, e.g. a glass slice, or a conductive material.

15 Said substrate can comprise a patterned conductive layer. Particularly, in case said substrate is a partly processed wafer or slice; at least a part of the active and/or passive devices can already be formed and/or at least a part of the structures interconnecting these devices can be
20 formed.

[0036] Preferably this conversion is performed at low temperatures, preferably 600°C or below, in an oxygen-containing plasma.

[0037] For the purpose of this disclosure, plasma
25 should be understood as a conventional plasma such as a reactive ion etch (RIE) plasma or a chemical vapour deposition (CVD) plasma, or a plasma afterglow. By exposing said carbide-silicon layer to an oxygen-containing plasma, energy is given to the oxygen containing species, such that
30 carbide-silicon is at least partly converted into oxide-silicon. This energy can be e.g. thermal energy or kinetic energy, e.g. by the formation of ions.

[0038] In an embodiment of the invention the conversion from a part of the carbide-silicon layer to an
35 oxide-silicon layer can be performed by exposing the carbide-silicon layer to an oxygen-containing reactive ion etch (RIE) plasma. Particularly, the substrate including the carbide-silicon layer can be introduced in a

pressurized chamber of a plasma-etch tool. The pressure can be lower than 3 Torr and preferably between 1 mTorr and 1 Torr. The temperature in said chamber can be 300°C or below; or preferably below 100°C. This temperature can also
5 be in the range from -20°C to 100°C. Preferably, said temperature is about room temperature. The energy of the RIE plasma can be between 1 eV and 500 eV, such that ionic species can be formed.

[0039] In another embodiment, the conversion from a
10 part of the carbide-silicon layer to an oxide-silicon layer can be performed by exposing the carbide-silicon layer to an oxygen-containing CVD plasma. The substrate including the carbide-silicon layer can be introduced in a pressurised chamber of a chemical vapour deposition tool.
15 The pressure can be, but is not limited hereto, higher than 5 Torr, e.g. 10 Torr. The temperature can be in the range between 250°C and 550°C, preferably in the range between 350°C and 500°C.

[0040] In yet another embodiment of the invention,
20 the conversion from a part of the carbide-silicon layer to an oxide-silicon layer can be performed by exposing the carbide-silicon layer to an oxygen-containing plasma afterglow. Particularly, the substrate including the carbide-silicon layer can be introduced in a pressurised
25 chamber of a plasma-etch tool. Said plasma afterglow can be characterised, but is not limited hereto, by a pressure in the range from 0.02 Torr to 3 Torr, and in the range between 0.2 Torr and 1.5 Torr and preferably between 0.75 Torr and 1.25 Torr, e.g. about 0.85 Torr or 1.1 Torr. The
30 flow of the oxygen containing substance can be lower than 10000 Sccm and preferably, but not limited hereto, about 4000 Sccm.

[0041] The temperature in said chamber is preferably
35 600°C or below. This temperature can also be in the range from 100 to 600°C and also in the range from 200 to 400°C and also in the range from 200 to 300°C. This temperature is preferably, but not limited hereto, about 230°C.

[0042] Said removal step is performed by exposing the oxide silicon layer to a wet or dry etch. Said wet etch can comprise, but is not limited hereto, diluted HF, diluted BHF or wet etchants comprising HF or BHF. Said dry
5 etch can be a dry etch chemistry comprising a fluorine source.

[0043] In a preferred embodiment, this conversion is performed at low temperatures, preferably 600°C or below, in an oxygen-containing plasma, particularly in a plasma
10 afterglow. The carbide-silicon layer is exposed to an oxygen-containing plasma afterglow at a temperature of 600°C or below. Particularly a temperature in the range from 200°C to 400°C can be used. In this temperature range, conversion of the exposed part of a carbide-silicon layer
15 can be obtained through interaction of atomic oxygen or an oxygen radical or an ionic oxygen or another oxygen containing oxidising species with the carbide-silicon layer. Generation of these reactive species can be obtained by generating a plasma in appropriate gas mixtures. As an
20 example, the oxidation of a carbide-silicon layer, particularly amorphous hydrogenated silicon carbide, obtained in the afterglow of an O₂-discharge is discussed below. The example is referred to as example 1 (see also Fig. 1 and Fig. 2). An oxygen containing plasma is a plasma
25 comprising at least oxygen. An oxygen containing plasma can comprise, but is not limited hereto, at least oxygen and one of the group consisting of N₂, C_xF_y, SF_z, or another halogen source.

30 EXAMPLE 1

Afterglow oxidation of amorphous hydrogenated silicon carbide

[0044] The carbide-silicon layers (1) (2) were
35 formed through plasma enhanced deposition on Si wafers. Thereafter, the carbide-silicon layers (1) (2) on these wafers are submitted to an O₂ / N₂ plasma afterglow for different times at a pressure of 1.1 Torr. The O₂-flow is

4000 sccm, while the N₂-flow is 200 sccm. The wafer temperature was maintained at about 230°C. Different samples were submitted for different process times, all in the range from 2 to 8 minutes. After oxidation, samples
5 were etched in a 2% HF mixture for 5 minutes (4). Ellipsometric measurements were performed after deposition of the film (3), after oxidation and after wet etching (5) in the diluted HF solution.

[0045] From these measurements, the following
10 observations can be made:

- a. Exposure of carbide-silicon to an oxygen-containing ambient in the medium temperature range, i.e. the range from 100°C to 600°C, converts the carbide-silicon to a material showing different optical
15 properties
- b. The change of the ellipsometric parameters depends on the exposure time.
- c. The converted material can be removed in 2% HF solution
- 20 d. The amount of removed material, i.e. the thickness of the converted layer, is depending on the exposure time. More material is removed for longer plasma exposure times.
- e. After removal of the converted layer, identical
25 optical properties as for the pristine carbide-silicon are found.
- f. Carbide-silicon remains substantially unaffected when subjected to a 2% HF solution (Fig. 2). Fig.2 (21) clearly shows that the converted part of the carbide-silicon layer is removed in the first twenty seconds,
30 while the etch process has no effect on the unconverted part of the carbide-silicon layer.

[0046] This example clearly shows the possibility of converting carbide-silicon layers to oxide-silicon layers.
35 Dependent on the exposure times, the exposed layer of a carbide-silicon layer can be converted partly or completely. This converted layer can be removed e.g. in a HF based solution. The conversion step and the removal step

are subsequently repeated for a number of times until said carbide-silicon layer is substantially removed. In case the conversion is complete, after etching the layer underlying the original carbide-silicon layer is exposed. In the
5 latter case the removal process is selected such that it selectively removes the oxide-silicon layer at least with respect to said underlying layer.

[0047] In another embodiment of the invention, at least a part of a carbide-silicon layer is exposed to an
10 oxygen-containing RIE plasma. Using an RIE plasma instead of a plasma afterglow can have some benefits including the possibility to perform the conversion at low temperatures, e.g. at room temperature. Moreover, besides the potential benefit of the lower temperature, the conversion can be
15 performed anisotropically in an RIE plasma which is a huge benefit for in-situ conversion especially for fabricating interconnect and dielectric structures such as e.g. a damascene or dual-damascene metallization scheme.

[0048] Alternatively, instead of exposing carbide-silicon to an oxygen-containing plasma, one can also expose
20 carbide-silicon to a nitrogen-containing plasma in order to convert the carbide-silicon to a nitride-silicon. At least for the purpose of this disclosure a nitride-silicon layer is a layer composed of at least Si and N, e.g. silicon
25 nitride or of Si, N and a smaller fraction of C. In case of this nitridation, the converted carbide-silicon layer can be removed using e.g. Phosphoric acid. By doing so, the obtained Si_3N_4 can be removed selective both to silicon (di)oxide and silicon. This method can for instance be used
30 in integration schemes where the carbide-silicon layers needs to be removed selective to silicon (di)oxide present on the wafer surface.

[0049] In yet another embodiment of the invention, an integrated circuit is disclosed wherein a carbide-
35 silicon layer is used as an etch stop layer and as a diffusion barrier layer between a conductive layer and the surrounding dielectric. The conductive layer can be deposited on a semiconducting layer. The conductive layer

(43) can be a pure metal or a metal alloy of the group of metals consisting of Al, Cu, W, Pt, Ag, Ni, Au, Co, Ti, Ta, or a Si-containing or other semiconductor-containing layer such as e.g. a silicide, a polysilicon or a silicon layer.

5 This conductive layer can also be a stack of a barrier layer, conductive or not, and a metal layer.

[0050] In an embodiment of the invention, an interconnect structure on a substrate having a surface with at least one exposed Si-containing layer, particularly a
10 PMD structure, is disclosed wherein a carbide-silicon layer is used as an etch stop layer and as a diffusion barrier layer between a silicide layer and the surrounding dielectric.

[0051] A major problem in PMD structures (see also
15 in Fig. 3) and particularly in the definition of contact holes, i.e. openings in the (multi-layer) dielectric, extending to the silicide layer, is the selectivity towards the silicide material. Silicide layers are thin layers having a low resistivity and a low contact resistance to an
20 adjacent silicon-containing layer as e.g. a Si substrate or a polysilicon or amorphous silicon layer.

[0052] A silicide layer comprises a compound comprising silicon and at least one of the group comprising Co, Ti, Ta, Nb, Ni, Pt and W. A silicide layer can be,
25 but is not limited hereto, a silicide-cobalt layers being defined as Co_xSi_y , x and y being positive numbers, e.g. CoSi_2 , or silicon-titanium layers being defined as Ti_xSi_y , x and y being positive numbers, e.g. TiSi_2 . In conventional schemes, as for instance in the silicides are used as etch
30 stop layers during the formation of contact holes. Many schemes use bi-level contacts or multi-level contacts, putting even higher requirements onto the selectivity of the contact etch process towards the silicide. Contact etch processes may show aspect ratio dependent etch rates
35 (slower etch rate with decreasing contact size) and thus aspect ratio dependent selectivity. Control of the selectivity for both shallow and deep contacts becomes very critical. In addition, the following trends are observed

nowadays which puts even some more emphasis on this selectivity :

a) Introduction of CMP inducing non-uniformity of the dielectric and hence requiring increased
5 over-etch time.

b) Reduction of the silicide thickness requiring ever increasing selectivity.

c) Introduction of shallow junctions being more sensitive for degradation effects and putting
10 stringent requirements on the maximum allowable silicide thickness.

[0053] All of these trends require better selectivity towards silicides and in fact, for some technologies, selectivity becomes the limiting factor.

15 [0054] A way to address the selectivity issue is the use of a so-called etch stop layer. Such a thin etch-stop layer is deposited at least on the silicide contact layers prior to the deposition of the pre-metal dielectric stack. A typical material being used as an etch stop layer is
20 silicon nitride. The contact etch process is set up to stop on or in the this silicon nitride layer. Afterwards, an additional etch step for controlled removal of the thin nitride layer is introduced. Advantages of this approach are the limited exposure of the silicides and/or silicon or
25 other substrate material to the etch plasma which, in principle allows better control of substrate material loss. The introduction of an etch stop layer can overcome the etch problems related to the topography of the dielectric layers to be etched and the effect of multi-level schemes,
30 particularly the simultaneous definition of shallow and deep contact holes. The set up of the contact etch and nitride removal process however is complicated. Dependent on the dielectrics used, the selectivity of the etch process of the dielectric towards nitride can be too
35 limited, especially when silicon (di)oxide is used as a dielectric. Moreover, the removal of nitride selective towards silicide is even a bigger problem.

- [0055] Besides the selectivity issue the etch-stop layer also has to be a good barrier layer amongst others to reduce the in-diffusion of contamination e.g. metal particles. In case silicon nitride is used as etch stop layer, then this layer needs careful optimisation towards better barrier properties and it can be expected that improvement in terms of in-diffusion of contamination will result in a more difficult etch and therefore negatively influences the selectivity issue.
- 10 [0056] Further according to this embodiment of the invention a carbide-silicon layer is introduced as an etch stop layer having excellent barrier properties. Due to its intrinsic high chemical stability it is almost impossible to remove it selectively towards silicide. However due to
- 15 the conversion method of the present convention it can be converted in-situ at sufficient low temperature in an oxide-silicon, which on its turn can be easily removed selectively towards the silicide. For a typical oxide etch process (e.g. CF_4/CHF_3), the selectivity of oxide etch
- 20 towards SiC is better than the selectivity towards nitride. For less standard chemistries, the same behaviour has been demonstrated. In addition, the selectivity of oxide etch towards silicide is better than the selectivity of nitride etch towards silicide.
- 25 [0057] In Fig. 3 an interconnect structure on a substrate (31) having a surface with at least one exposed Si-containing layer (32), particularly a PMD structure, is disclosed. An exposed Si-containing layer can be a Si-containing substrate layer (32), such as e.g. a source, a
- 30 drain or a collector region, or a polysilicon or amorphous silicon region, such as e.g. a gate region or an extrinsic emitter or base region. The substrate can be a partly processed or a pristine wafer or slice of a semiconductive material, like Si or GaAs or Ge, or an insulating material,
- 35 e.g. a glass slice. Said substrate can comprise a patterned dielectric layer and/or a patterned amorphous silicon or polysilicon layer. Particularly, in case said substrate is

a partly processed wafer or slice; at least a part of the active and/or passive devices can already be formed.

[0058] This PMD structure further comprises :

a silicide layer (33) on said exposed
5 Si-containing layer;

at least one dielectric layer (34) on said surface of said substrate having at least one opening (36), said opening extending through said dielectric layer to thereby define an exposed part of said silicide layer; and

10 a carbide-silicon layer (35) being formed at least on said silicide layer and being positioned between said dielectric layer and said silicide layer adjacent to said exposed part of said silicide layer.

[0059] A dielectric layer can be a ceramic silicon
15 oxide, nitride or oxynitride layer, fluorinated or not, or an organic polymer layer selected from the group consisting of the benzocyclobutarenes, i.e. benzocyclobutene (BCB) commercially available as Cyclotene 5021TM, poly arylene ether, i.e. FLARETM II, aromatic hydrocarbon, i.e. SILKTM,
20 and polyimides. Such an organic polymer layer can be in-situ fluorinated. Also porous (inorganic) dielectric layers can be used as for instance e.g. the xerogels.

[0060] Typical examples of silicides are silicides of a refractory metal such as Ti, Ta, Co, Mb, Ni and Pt.

25 [0061] In Fig 4, according to a further embodiment of the invention, some of the process steps to obtain an interconnect structure, including a PMD structure and inter or intra metal structures (IMD), are depicted :

a) As a first process step (step a)), a
30 carbide-silicon layer (45) with a thickness of typically about 50nm is deposited on a substrate (41), i.e. at least on the exposed conductive layers (42). Preferably however, a blanket deposition of this insulating carbide-silicon layer is performed. This carbide-silicon layer which is at
35 the same time an etch-stop layer and a barrier layer prevents the in-diffusion of contamination. The conductive layer (43) can be a pure metal or a metal alloy of the group of metals consisting of Al, Cu, W, Pt, Ag, Ni, Au,

Co, Ti, Ta, or a Si-containing or other semiconductor-containing layer such as e.g. a silicide, a polysilicon or a silicon layer. This conductive layer can also be a stack of a barrier layer, conductive or not, and a metal layer.

5 The substrate can be a partly processed or a pristine wafer or slice of a semi-conductive material, like Si or Ga As or Ge, or SiGe or an insulating material; e.g. a glass slice, or a conductive material. Said substrate comprises a (patterned) conductive layer. Particularly, in case said
10 substrate is a partly processed wafer or slice; at least a part of the active and/or passive devices can already be formed and/or at least a part of the structures interconnecting these devices can be formed;

b) After the deposition of the carbide-
15 silicon layer, at least one dielectric layer (44) is formed thereon. Then, at least one opening is formed (step b)) in the dielectric layer(s) extending through the dielectric layer(s) to thereby expose a part of the carbide-silicon layer formed on the conductive layer. This opening is
20 formed preferably using a dry etch sequence using at least a patterned resist layer on top the dielectric layers as a mask. Because the carbide-silicon acts as an etch-stop layer, there is a large process window available for this contact etch process;

25 c) The exposed part of the carbide-silicon layer in the opening can now be at least partly converted in-situ into oxide-silicon by exposure to an oxygen-containing plasma; and

d) Thereafter, the oxide-silicon layer in
30 said opening (and simultaneously the resist) can be removed selectively. The sequence of steps c) and d) can be executed repeatedly till the underlying conductive layer is exposed.

[0062] There are several alternatives possible for
35 this sequence of steps a) to d). The invention is in no way restricted to this particular sequence.

[0063] As a first alternative one can opt for a complete conversion of the carbide-silicon (step c)). In

this case, the oxide-silicon layer can be removed selectively to said conductive layer to thereby expose a part of said conductive layer.

[0064] As a further alternative, prior to the
5 conversion of the carbide-silicon (step c)), a barrier layer can be formed at least on the side walls of the openings in the dielectric layers(s) to protect the dielectric stack. In case the subsequent conversion/removal of the carbide silicon is executed by means of exposure in
10 an anisotropic oxygen-containing RIE, plasma, then one can also opt for a carbide-silicon layer as barrier layer on the side walls of the openings.

EXAMPLE 2

15 An exemplary processing scheme further according to the method of the present invention

[0065] First a SiC layer is deposited on a Si-wafer comprising patterned oxide layers and exposed conductive
20 layers of TiSi_2 directly on the Si wafer and of TiSi_2 on patterned polysilicon layers. Then oxide layers are deposited defining a dielectric stack. A resist is formed and patterned atop this dielectric stack. Next the Si-wafer is introduced in an oxide etch chamber for the contact etch
25 defining the openings in the oxide stack. The etch stops on the SiC layer. The exposed part of the SiC layer is in-situ converted into silicon dioxide using a low temperature oxygen-containing plasma afterglow, while at the same time the resist is removed. The same oxide etch chamber is used.
30 Finally, the converted SiC, i.e. the silicon dioxide is removed selectively towards the TiSi_2 in the same oxide etch chamber. Some advantages of using SiC instead of e.g. silicon nitride include: full in-situ processing, reduced silicide loss, good contact resistance and yield since
35 standard chemistry can be used, and improved barrier properties. SiC can be used in this processing scheme as alternative material towards nitride.

CLAIMS

1. A method for removing at least partly an exposed part of a carbide-silicon layer formed on a substrate comprising the steps of :

- converting at least partly said exposed part of said carbide-silicon layer into an oxide-silicon layer by exposing said carbide-silicon layer to an oxygen containing plasma; and
- removing said oxide-silicon layer from said substrate.

2. A method as recited in claim 1, wherein said conversion step and said removal step are subsequently repeated for a number of times until said carbide-silicon layer is substantially removed.

3. A method as recited in claim 1 or 2, wherein said carbide-silicon layer comprises at least one of the group consisting of silicon carbide, silicon oxycarbide, nitrided silicon carbide, nitrided silicon oxycarbide, hydrogenated silicon carbide, hydrogenated silicon oxycarbide, hydrogenated nitrided silicon carbide and hydrogenated nitrided silicon oxycarbide.

4. A method as recited in any one of the preceding claims, wherein said oxide-silicon layer comprises at least one of the group consisting of silicon dioxide, silicon dioxide with a smaller fraction of C, silicon dioxide with a smaller fraction of N and C, silicon dioxide with a smaller fraction of N, hydrogenated silicon dioxide, hydrogenated silicon dioxide with a smaller fraction of C, hydrogenated silicon dioxide with a smaller fraction of N and C and hydrogenated silicon dioxide with a smaller fraction of N.

5. A method as recited in any one of the claims 1 to 4, wherein said oxygen containing plasma is an oxygen containing reactive ion etch plasma.

6. A method as recited in claim 5, wherein
5 said conversion step is performed at a temperature in the range between -20°C and 100°C.

7. A method as recited in claim 5, wherein said conversion step is performed at a room temperature.

8. A method as recited in any one of the
10 claims 1 to 4, wherein said oxygen containing plasma is an oxygen-containing chemical vapour deposition plasma.

9. A method as recited in claim 8, wherein said conversion step is performed at a temperature in the range between 350°C and 500°C.

15 10. A method as recited in any one of the claims 1 to 4, wherein said oxygen containing plasma is an oxygen containing plasma afterglow.

11. A method as recited in claim 10, wherein said conversion is performed at a temperature in the range
20 between -200°C and 400°C.

12. A method as recited in any one of the claims 1 to 11, wherein said step of removing said oxide-silicon layer from said substrate is done by applying one of the group consisting of a fluorine based dry etch, HF
25 based wet etch, BHF based wet etch and HF/BHF based wet etch to the substrate.

13. A method for fabricating an integrated circuit on a substrate having a surface with at least one conductive layer on a semiconducting layer comprising the
30 steps of :

- forming a carbide-silicon layer on top of at least said conductive layer,

- depositing at least one dielectric layer on at least said carbide-silicon layer,

- forming at least one opening in said dielectric layer extending through said dielectric layer to
5 expose a part of said carbide-silicon layer formed on said conductive layer,

- converting at least partly said exposed part of said carbide-silicon layer in said opening into an silicon-oxygen layer by exposing said exposed part of said
10 carbide-silicon layer in said opening to an oxygen-containing plasma, and

- removing said oxide-silicon layer in said opening.

14. A method as recited in claim 13, wherein
15 said conductive layer is a silicide layer.

15. A silicide layer as recited in claim 14, wherein said silicide is a compound comprising silicon and at least one of the group comprising Co, Ti, Ta, Co, Mb, Ni, Pt and W.

20 16. A method as recited in claim 13, wherein said conductive layer is one of the group consisting of a polysilicon layer and an amorphous silicon layer.

17. A method as recited in any one of the claims 13 to 16, wherein said conversion step and said
25 removal step are subsequently repeated for a number of times until at least a part of said conductive layer is exposed.

18. A method as recited in any one of the claims 13 to 17, wherein said carbide-silicon layer
30 comprises at least one of the group consisting of silicon carbide, silicon oxycarbide, nitrided silicon carbide, nitrided silicon oxycarbide, hydrogenated silicon carbide, hydrogenated silicon oxycarbide, hydrogenated nitrided

silicon carbide and hydrogenated nitrided silicon oxycarbide.

19. A method as recited in any one of the claims 13 to 18, wherein said oxide-silicon layer comprises
5 at least one of the group consisting of silicon dioxide, silicon dioxide with a smaller fraction of C, silicon dioxide with a smaller fraction of N and C, silicon dioxide with a smaller fraction of N, hydrogenated silicon dioxide, hydrogenated silicon dioxide with a smaller fraction of C,
10 hydrogenated silicon dioxide with a smaller fraction of N and C and hydrogenated silicon dioxide with a smaller fraction of N.

20. An integrated circuit on a substrate having a surface with at least one conductive layer
15 comprising :

- a conductive layer deposited on a semiconducting layer,
- at least one dielectric layer having at least one opening extending through said dielectric layer
20 to expose at least a part of said conductive layer, and
- a carbide-silicon layer being formed at least on said conductive layer and being positioned between said dielectric layer and said conductive layer adjacent to said exposed part of said conductive layer.

21. An integrated circuit as recited in claim 20, wherein said conductive layer is a silicide layer.

22. An integrated circuit as recited in claim 21, wherein said silicide is a compound comprising
30 silicon and at least one of the group consisting of Co, Ti, Ta, Co, Nb, Ni, Pt and W.

23. An integrated circuit as recited in claim 20, wherein said conductive layer is one of the group

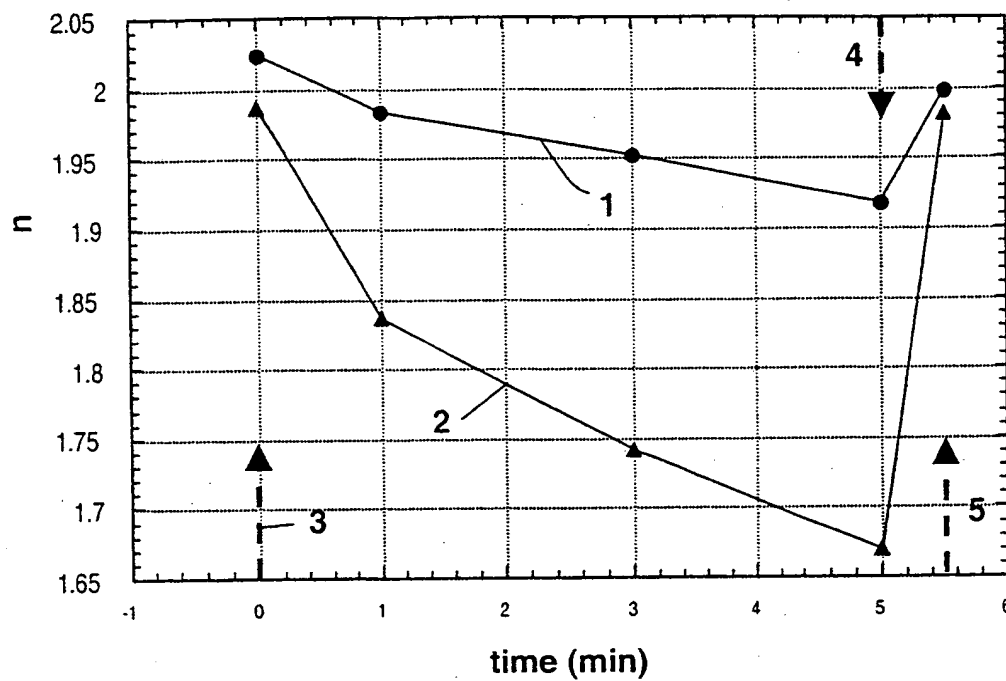
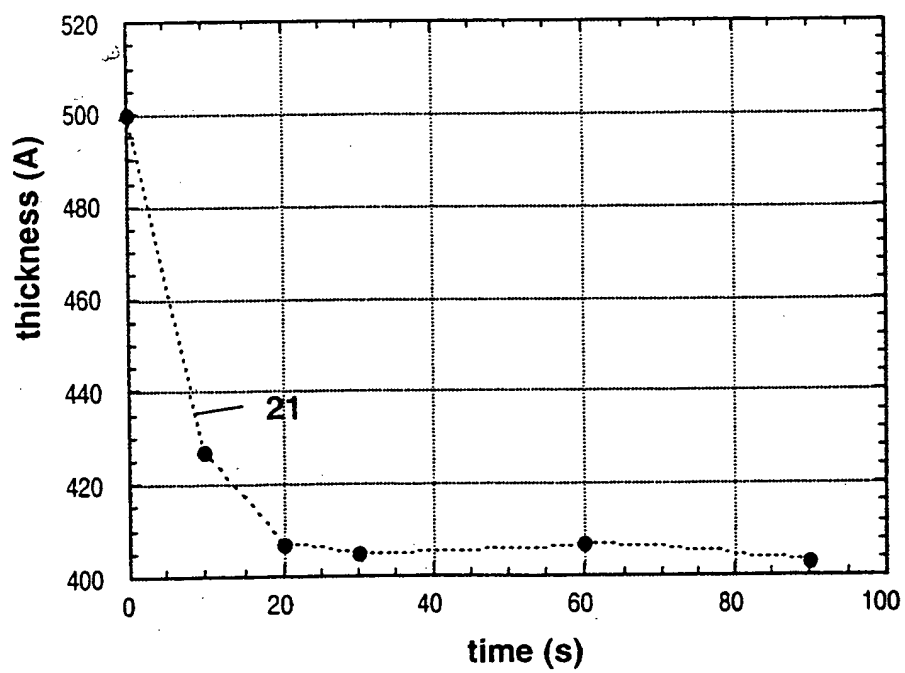
consisting of a polysilicon layer and an amorphous silicon layer.

24. An integrated circuit as recited in any one of the claims 20 to 23, wherein said semiconducting
5 layer is one of the group consisting of a silicon layer, a Ga As layer, a Ge layer and a SiGe layer.

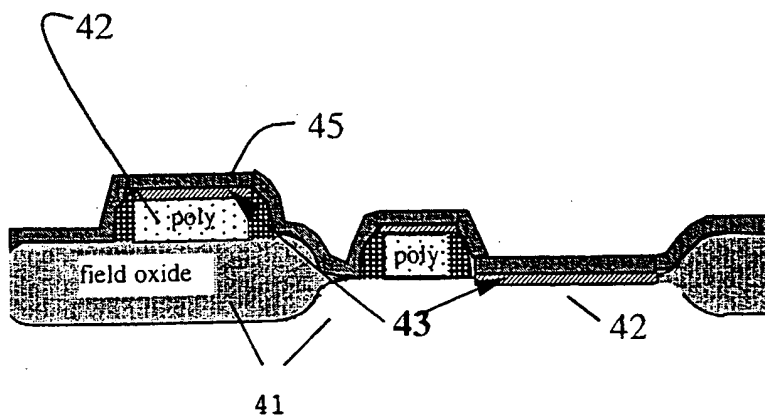
25. An integrated circuit as recited in any one of the claims 20 to 24, wherein said carbide-silicon layer comprises at least one of the group consisting of
10 silicon carbide, silicon oxycarbide, nitrided silicon carbide, nitrided silicon oxycarbide, hydrogenated silicon carbide, hydrogenated silicon oxycarbide, hydrogenated nitrided silicon carbide and hydrogenated nitrided silicon oxycarbide.

15 26. An integrated circuit as recited in any one of the claims 20 to 25, wherein said oxide-silicon layer comprises at least one of the group consisting of silicon dioxide, silicon dioxide with a smaller fraction of C, silicon dioxide with a smaller fraction of N and C,
20 silicon dioxide with a smaller fraction of N, hydrogenated silicon dioxide, hydrogenated silicon dioxide with a smaller fraction of C, hydrogenated silicon dioxide with a smaller fraction of N and C and hydrogenated silicon dioxide with a smaller fraction of N.

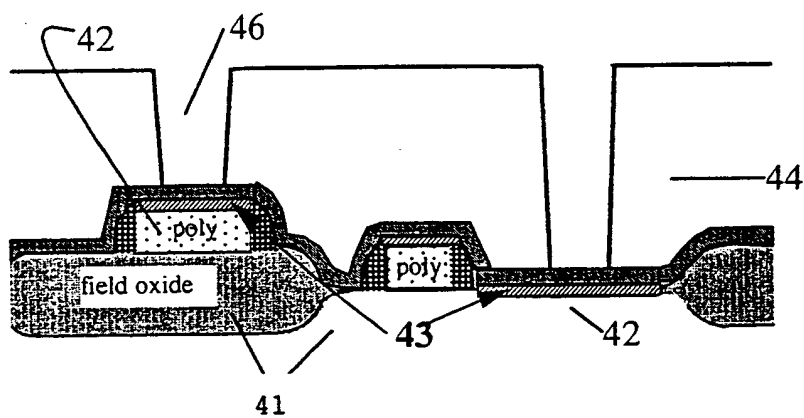
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FIG. 1FIG. 2

Step a)



Step b)



Step c) and d)

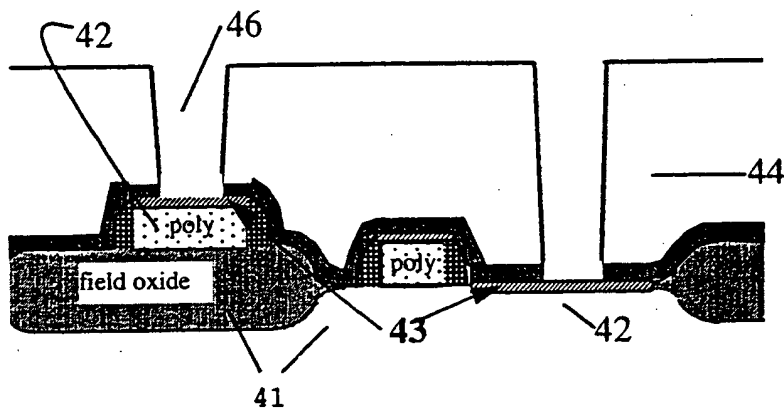


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 00/00045

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/04 H01L21/311

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 948 461 A (CHATTERJEE DILIP K) 14 August 1990 (1990-08-14)	1,3-5,8, 12
Y	column 2, line 61 -column 3, line 4 ---	13
X	EP 0 725 440 A (DOW CORNING) 7 August 1996 (1996-08-07) cited in the application	20
Y	the whole document ---	13
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 02, 31 March 1995 (1995-03-31) & JP 06 314791 A (FUJI ELECTRIC CO LTD), 8 November 1994 (1994-11-08) abstract --- -/--	1,12,13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search

8 September 2000

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 apo nl,
Fax: (+31-70) 340-3016

Authorized officer

Königstein, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 00/00045

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 571 374 A (THERO CHRISTINE ET AL) 5 November 1996 (1996-11-05) the whole document	1,13
X	NINOMIYA S ET AL: "CHEMICAL ETCHING OF THERMALLY-GROWN SiO ₂ FILMS ON SiC STUDIED BY SPECTROSCOPIC ELLIPSOMETRY" JAPANESE JOURNAL OF APPLIED PHYSICS, JP, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, vol. 33, no. 4A, PART 01, 1 April 1994 (1994-04-01), pages 1833-1834, XP000487628 ISSN: 0021-4922 the whole document	1,12
A	CHAPPEL D C ET AL: "HIGH FREQUENCY CV CHARACTERISTICS OF PLASMA OXIDISED SILICON CARBIDE" ELECTRONICS LETTERS, GB, IEE STEVENAGE, vol. 33, no. 1, 2 January 1997 (1997-01-02), pages 97-98, XP000692510 ISSN: 0013-5194 the whole document	
X	VON MUNCH W ET AL: "Thermal oxidation and electrolytic etching of silicon carbide" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, MAY 1975, USA, vol. 122, no. 5, pages 642-643, XP000939210 ISSN: 0013-4651 the whole document	1
X	WOLF R ET AL: "Reactive ion etching of 6H-SiC in SF ₆ /sub 6//O/sub 2/ and CF ₄ /sub 4//O/sub 2/ with N/sub 2/ additive for device fabrication" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, MARCH 1996, ELECTROCHEM. SOC, USA, vol. 143, no. 3, pages 1037-1042, XP000939211 ISSN: 0013-4651 the whole document	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BE 00/00045

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4948461 A	14-08-1990	NONE	
EP 0725440 A	07-08-1996	US 5818071 A JP 8250594 A	06-10-1998 27-09-1996
JP 06314791 A	08-11-1994	NONE	
US 5571374 A	05-11-1996	EP 0767490 A JP 9129622 A	09-04-1997 16-05-1997

